

Madelung Energy of the Valence Skipping Compound BaBiO₃

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Several elements show valence skip fluctuation, for instance, Tl forms the compounds in valence states +1 and +3, and Bi forms in +3 and +5 states. This kind of fluctuation gives rise to a negative effective attractive interaction and the Kondo effect. In the compounds of valence skipping elements, the carrier doping will induce superconductivity with high critical temperature. For example, Ba_{1-x}K_xBiO₃ shows high T_c which is unlikely from the conventional electron-phonon mechanism. The reason for the missing of some valence states in such valence skip compounds remains a mystery. We have performed the evaluation of the Madelung potential for BaBiO₃, and have shown for the first time that charge-ordered state is stabilized if we take into account the polarization of the oxygen charge. We argue that the effective Coulomb interaction energy U may be negative evaluating the local excitation energy.

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In the periodic table more than ten elements show valence skip in all the compounds they form. Tl and In form the compounds with the valence states +1 and +3, Bi and Sb form with +3 and +5 states, and Pb and Sn with +2 and +4 valence states. It is reasonable to expect a new microscopic physics behind this phenomenon. The reason for missing valence states for these elements still remains a mystery[1, 2, 3]. The valence skipping leads to the Hubbard type model with the negative- U attractive interaction. Since the attractive interaction possibly promotes superconductivity, the carrier doping may induce superconductivity with relatively high T_c . For example, Ba_{1-x}K_xBiO₃ shows high T_c which is unlikely from the conventional electron-phonon interaction. A substitution of Ba with K for the compound BaBiO₃ provides superconductivity with T_c exceeding 30K[4, 5, 6, 7, 8]. Ba_{1-x}K_xBiO₃ is the perovskite three-dimensional superconductor with clear s-wave gap. The parent compound BaBiO₃ is an insulator though BaBiO₃ should be a metal according to the band theory[9, 10].A band-calculation within the local-density approximation (LDA) leads to a (semi)metallic ground state of BaBiO₃[11],even under the lattice distortion found in the neutron-diffraction experiments. The average formal valence state of Bi is +4. The insulating state of BaBiO₃ would have spin 1/2 at Bi site if Bi with +4 were allowed. BaBiO₃ is, however, the insulator with a charge density wave (CDW) gap of the order of 2eV. The valence states +3 and +5 form the CDW state with average charge +4. The substitution of K for Ba induces carriers as doped holes leading to superconductivity, which is reminiscent of the phase diagram of cuprate high temperature superconductors. Since the high critical temperature found in Ba_{1-x}K_xBiO₃ may be unlikely from the conventional electron -phonon mechanism, one can expect that the negative- U attractive interaction would cooperate in promoting superconductivity[12, 13, 14].

The valence skip is important in the study of a charge Kondo effect[15] as well as valence-fluctuation induced superconductivity[16]. A superconductor Pb_{1-x}Tl_xTe with $T_c = 1.4$ K[17] is reasonably expected to belong to the same category. The mother compound PbTe is a small gap semiconductor. For Tl concentrations up to the solubility limit 1.5 percent, the material shows superconductivity with a remarkably high T_c as a low carrier metal. Tl impurities as negative- U centers could leads to superconductivity and at the same time Kondo effect as a charge analog[15, 18].

The purpose of this paper is to investigate the mystery of missing valence states evaluating the intra-atomic energy for Bi⁴⁺ ion. In general, the total energy is the sum of the one-body potential energy and the interaction energy. The Coulomb interaction is primarily important for the insulator BaBiO₃. The curvature of the total energy as a function of the valence n , which is closely related with the intra-atomic energy U , may be presumably changed due to the Coulomb interaction. In the way stated we calculate the Madelung energy of BaBiO₃. Let q_i be the charge on the site i , the total Coulomb energy is

$$E = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where r_{ij} is the distance between the sites i and j . If we define the potential at the site i as

$$V_i = \sum_{j \neq i} \frac{q_j}{r_{ij}}, \quad (2)$$

the total Coulomb energy is

$$E = \frac{1}{2} \sum_i q_i V_i. \quad (3)$$

The potential V_i , called the Madelung potential, is evaluated using the Ewald method.[19, 20] We calculated

the Madelung potential and the total energy for the valence skipping compound BaBiO₃. We assign the formal charges as

$$(A) \text{ Ba : } 2+, \text{ Bi : } 4+, \text{ O : } 2- \quad (4)$$

$$(B) \text{ Ba : } 2+, \text{ Bi(1) : } 3+, \text{ Bi(2) : } 5+, \text{ O : } 2- \quad (5)$$

where in the latter case the charge density wave with valences 3+ and 5+ is assumed. Let us denote the number of Ba atoms as N_A , then the number of Bi and O atoms are N_A and $3N_A$, respectively. The total Madelung energy for the case (A) is

$$\begin{aligned} E_{Madel} &= \frac{1}{2}(N_A q_{Ba} V_{Ba} + N_A q_{Bi} V_{Bi} + 3N_A q_O V_O) \\ &= \frac{N_A}{2}(q_{Ba} V_{Ba} + q_{Bi} V_{Bi} + 3q_O V_O), \end{aligned} \quad (6)$$

where $q_{Ba} = 2$, $q_{Bi} = 4$ and $q_O = -2$. For the case (B) the total Madelung energy is

$$\begin{aligned} E_{Madel} &= \frac{N_A}{2}(q_{Ba} V_{Ba} + \frac{1}{2}q_{Bi(1)} V_{Bi(1)} + \frac{1}{2}q_{Bi(2)} V_{Bi(2)} \\ &\quad + 3q_O V_O), \end{aligned} \quad (7)$$

for $q_{Ba} = 2$, $q_{Bi(1)} = 3$, $q_{Bi(2)} = 5$ and $q_O = -2$. The intra-atomic repulsion energy U can be calculated if the total energy is obtained. For the valence n , the energy U is defined as

$$U_n = E_{n+1} + E_{n-1} - 2E_n, \quad (8)$$

where E_i is the energy of the valence i state. The U for Bi⁴⁺ per two bismuth atoms has been estimated from the measured ionization energies of the elements as[1]

$$U_{4+} = E_{ion}(Bi^{3+}) + E_{ion}(Bi^{5+}) - 2E_{ion}(Bi^{4+}) = 10.7 \text{ eV}. \quad (9)$$

Here $E_{ion}(Bi^{n+})$ is the ionization energy of the element Biⁿ⁺. This estimated value is quite large although it is smaller than for Bi³⁺ ($U_{3+} = 19.7 \text{ eV}$) and Bi⁵⁺ ($U_{5+} = 32.3 \text{ eV}$). Thus the simple estimate results in the positive U .

We compare the total energy of the uniform state (A) and the ordered CDW state (B), where the total energy is the sum of the total Madelung energy and the one-body (ionic) potential energy. The total energy difference is

$$\begin{aligned} \Delta E &= E(Ba_2^{2+} Bi^{3+} Bi^{5+} O_6^{2-}) - E(Ba_2^{2+} Bi^{4+} Bi^{4+} O_6^{2-}) \\ &\quad + E_{ion}(Bi^{5+}) + E_{ion}(Bi^{3+}) - 2E_{ion}(Bi^{4+}), \end{aligned} \quad (10)$$

where $E(Ba_2^{2+} Bi^{3+} Bi^{5+} O_6^{2-})$ and $E(Ba_2^{2+} Bi^{4+} Bi^{4+} O_6^{2-})$ are the total Madelung energies per two BaBiO₃'s, respectively. The charge-ordered state is stabilized if ΔE is negative. The Madelung potential V_a ($a=\text{Ba}, \text{Bi}$ and O) are shown in the Table I where we use the convention that the potential V_i is negative for the positive charge $q_i > 0$. The total potential energy per BaBiO₃, E_{tot}/N_A , is -81.95 eV for

(A) and -83.40 eV for (B), respectively, which are shown in the first and second rows of the Table I. Apparently the case (B) with the charge density wave has the lower energy. From these values, we obtain $\Delta E = 7.8 \text{ eV}$ which is still positive. It is now important to notice that the ΔE is reduced if we consider the movement of the oxygen ions. The neutron diffraction demonstrated that the Bi ions occupy two crystallographically inequivalent sites with different Bi-O bond lengths[21]. It has been reported by the neutron diffraction experiment that the oxygen atoms are out of the center of two Bi ions by 4 percent of the Bi-O bond length due to lattice relaxation[10] (see Fig.1). Thus it is reasonable to move the positions of oxygen atoms with different Bi-O bond lengths in calculating the Madelung potential. In order to take into account the polarization of electrons of oxygen atoms, we have further moved the center of point charges more than reported by the neutron diffraction. It is plausible to assume that the center of the negative charges is more close to the neighboring positive charges Bi⁵⁺ than the nucleus of the atom. The evaluated results are shown in the Table I, and are also shown in Fig.2 as a function of the bond length. We found that the stabilization energy ΔE is reduced linearly as a function of the bond length O-Bi(1) and becomes negative for about 10 percent movement. This indeed shows the stability of the observed CDW state.

Moreover, chemical bonding between Bi and O ions can further stabilize this CDW state. Bi⁵⁺ ion can gain energy as the neighboring oxygen ions move toward it, lowering the energy of the oxygen states while raising the energy of the empty Bi s states, as compared to the Bi³⁺ where those s-states are occupied. We consider Bi⁵⁺ O₆²⁻ cluster and the three-parameter model shown by Mattheiss and Hamann[11] for simplicity. Adopting more precise five-parameter model does not change the result seriously. The relevant orbitals are $|Bi-s\rangle$ and $|O-A_{1g}\rangle = (|p_1\rangle + |p_2\rangle + |p_3\rangle + |p_4\rangle + |p_5\rangle + |p_6\rangle)/\sqrt{6}$ orbitals, where $|p_n\rangle$ ($n = 1, \dots, 6$) denotes the n -th oxygen p-orbital directing the Bi site. The secular equation is:

$$\begin{vmatrix} \Delta - \epsilon & t \\ t & -\epsilon \end{vmatrix} = 0 \quad (11)$$

here Δ is the difference of the one-electron orbital energy $\Delta = \epsilon(Bi-s) - \epsilon(O-A_{1g})$, and t is the effective transfer matrix $t = \sqrt{6}(sp\sigma)$. Using the well-known relation $(sp\sigma) \propto d^{-2}$ [25] and the distortion $x = 0.26$, then the energy gain (loss) by the distortion is 0.42 eV per electron for the bonding (antibonding) state. Since the Bi⁵⁺ site has two empty states, thus the total energy gain is 0.84 eV per Bi⁵⁺. On the other hand, Bi³⁺ ion cannot gain energy because there is no empty s-states. This effect apparently promotes forming the CDW state.

In the above discussion we only considered the insulating states. However, in the uniform BaBiO₃ the system may be metallic. In fact, band-calculations show that

uniform BaBiO₃ with no distortion and oxygen polarization should be metallic[11, 24]. The width of Bi6s band is about 4eV, and the Fermi level is just the middle of this band. Thus considering the small density of states at the bottom of this band, the average energy gain forming Bloch state is less than 1eV per electron. Each Bi⁴⁺ has one Bi6s electron, so that the total energy of the uniform state may go down less than 2eV. However, this value is not so large compared with the large energy gain of CDW state, and a further but little change of the negative charge, namely $x \sim 0.285$, can compensate this effect.

In order to further investigate the possibility of the negative U originating from the long-range Coulomb interaction, we consider a state excited locally from the CDW ground state: a (3+, 5+) Bi pair (e.g. Bi atoms at (0,0) and (0.5,0) in Fig.1) is changed into a (4+, 4+) pair in the CDW background. The excitation energy for this process is

$$E_{loc} = \frac{1}{2}(V_{Bi1} - V_{Bi2}) - \frac{1}{2} \sum_i q_i \left(\frac{1}{r_i} - \frac{1}{|\mathbf{r}_i - \mathbf{r}_B|} \right) - U(12)$$

Here $\mathbf{r}_B = a_1 \mathbf{e}_x$ denotes the position vector of Bi(2) at $\mathbf{e}_x = (0.5, 0, 0)$, and a_1 is twice the average Bi-Bi distance ($a_1 = 8.700\text{\AA}$). V_{Bi1} and V_{Bi2} are the Madelung potential at the Bi(1) and Bi(2) site, respectively. The first term in eq.(12) is the change of the Madelung energy of the Bi pair, and the second term denotes that of the Madelung potential of the other ions. The third term shows the energy gain of the ionic (one-body potential) energy for (3+, 5+) → (4+, 4+), shown in eq.(9). We performed the three-dimensional summation in real space for sites in the sphere of the radius R using the procedure of Harrison[22]. This summation converged well for $R \sim 200a_0$ (see Ref.22). We do not suffer from the usual extreme oscillation of the potential in this case because we only consider the difference of the Madelung energy. Thus we do not need to add the $-Q/R$ term in contrast to the method in Ref.22. In the case of the Bi(1)-O bond-length $x = 0.282$, the local excitation energy is $E_{loc} = 6.92 + 10.56 - 10.7 = 6.78\text{eV}$. Hence the CDW state is stable against local valence fluctuation. Rice and Sneddon examined the low-energy effective Hamiltonian for the CDW state of BaBiO₃ and insisted that there are two types of excitations[23]. One is the single-particle excitation mentioned above, and the other is the two-particle excitation which is an exchange of local charges as (3+, 5+) → (5+, 3+). The excitation energy for (3+, 5+) → (5+, 3+) is extremely large because the second

term of eq.(11) is twice as large as the process (3+, 5+) → (4+, 4+). From the definition of U_n in eq.(8), the quantity $U_{4+}^{local} \equiv -E_{local}$ resembles the intra-atomic energy. The value $U_{4+}^{local} = -6.78\text{eV}$ seems too large as the 'negative' U ; the high dielectric constant and doped carriers, however, may reduce E_{loc} .

In summary, we have evaluated the Madelung potential for the valence skipping compound BaBiO₃ using the Ewald method. The total energy of the charge-ordered

TABLE I: Madelung potential in units of eV. The total electrostatic energy E_{Mad}/N_A and the stabilization energy of the CDW state ΔE defined as eq.(10) are shown in units of eV. Note that E_{Mad}/N_A is for one BaBiO₃. The bond length between bismuth (1) and oxygen atoms is normalized as 0.25 when there is no lattice relaxation.

Bond length	Ba	Bi(1)	Bi(2)	O	E_{Mad}/N_A	ΔE
0.25	(A)	-8.917	-20.487	-20.487	10.685	-81.95
0.25	(B)	-8.917	-17.594	-23.379	10.685	-83.39
0.26	(A)	-8.908	-19.321	-21.789	10.661	-82.00
0.26	(B)	-8.908	-16.428	-24.681	10.867	-84.68
0.27	(A)	-8.881	-18.277	-23.244	10.589	-82.17
0.27	(B)	-8.881	-15.384	-26.136	11.003	-86.10
0.28	(A)	-8.838	-17.341	-24.874	10.465	-82.45
0.28	(B)	-8.838	-14.448	-27.766	11.093	-87.66
0.282	(A)	-8.827	-17.166	-25.223	10.434	-82.52
0.282	(B)	-8.827	-14.273	-28.115	11.105	-87.99
						-0.24

CDW state was calculated using the Madelung potential. We have evaluated the excitation energy for the local disorder (3+, 5+) → (4+, 4+). It was shown that the polarization of electrons reduces the energy difference ΔE and that an attractive 'negative' U is presumably realized if the center of the negative charges is moved from the center of the Bi-Bi bond by about 10 percent of the bond length. This indicates a possibility that the high critical temperature of Ba_{1-x}K_xBiO₃ is due to the valence-skipping induced negative U as well as the electron-phonon interaction. The results also suggests that the elements with high electronic polarizability have strong possibility to induce negative U . Since the Te²⁻ ion has high polarizability[19], a negative U induced superconductivity is likely present in Tl doped PbTe. The valence skip may provide a new idea for the material design of new superconductors.

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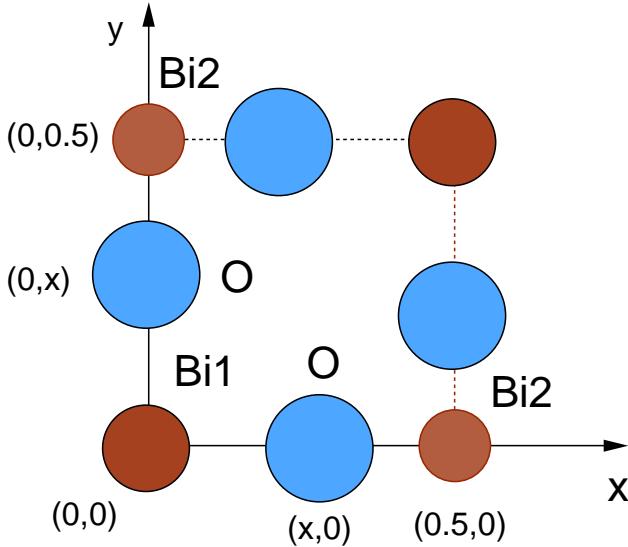


FIG. 1: The positions of bismuth and oxygen atoms in the plane of $z = 0$. Here we ignored the small tilting of BiO_6 octahedra.

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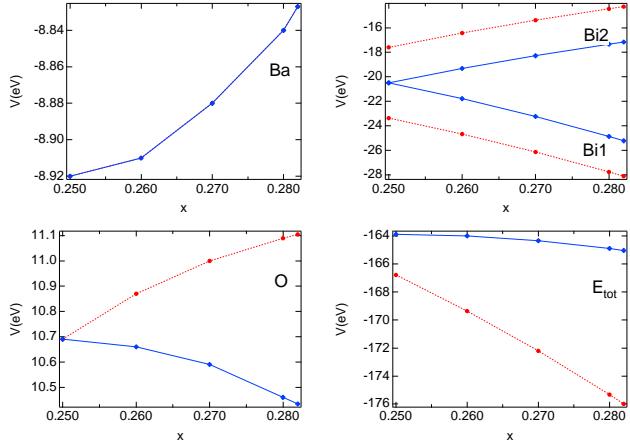


FIG. 2: The Madelung potential at the Ba, Bi and O sites and the total energy as a function of the bond length. The solid lines and the dotted lines correspond to the case (A) and the case (B) (with the charge density wave), respectively. The bond length is normalized as 0.25 when there is no lattice relaxation.